

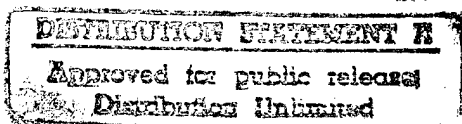
FEASIBILITY STUDY ON
ISOSTATIC PRESSING OF PYRRONES

By E. J. Bradbury and W. R. Dunnivant

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FOREWORD

This report was prepared by Battelle Memorial Institute under Contract NAS1-8245, "Feasibility Study on Isostatic Pressing of Pyrrones", for the Langley Research Center of the National Aeronautics and Space Administration. This work was administered under the technical direction of the Chemistry and Physics Branch of the Langley Research Center, with Captain Charles Johnson and Dr. George Sands acting as project managers.

ABSTRACT

< Studies were conducted on the fabricability of Pyrrone systems by room-temperature isostatic and conventional compression molding techniques. > Although uncured polymer powders could be isostatically compacted, completely cyclized polymers were not compacted at 100,000 psi even with liquid slip agents added. The low bulk density and noncompacting character of finely ground cured and partially cured Pyrrone powder prevented successful metal encapsulation for hot isostatic compaction. However, < the capability of the Pyrrones to be compression molded at elevated temperatures by dead-cure procedures (molding of fully cyclized polymer) was demonstrated and this fabrication method was emphasized. Correlations of conditions required to successfully mold Pyrrone pellets to various density and hardness values were developed. Molded Pyrrones were found to become quite brittle as their pellet densities increased. It was also shown that the molding procedure was complicated by an unfavorable thermal expansion relationship between the polymer and the mold. > Compressive stresses appear to be generated in mold restrained polymer during cooling such that serious cracking may occur. Some promise for improved recovery was shown by hot removal of the fabricated polymer from the mold. < High-speed grinding techniques were demonstrated to be satisfactory for sectioning and facing molded Pyrrone panels. >

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I. OBJECTIVE

Assist NASA in carrying out a preliminary feasibility study to determine if novel and technologically useful Pyrrone polymer compactions could be prepared by isostatic pressing techniques currently employed by the metals and ceramic industries. The scope of the objective was later expanded to include the exploration of compression molding conditions for Pyrrone resins.

II. INTRODUCTION

Recent advances in the development of heat-resistant polymers have provided a variety of new aromatic and aromatic-heterocyclic materials. Because of their ease of fabrication into certain end-item forms and a generally good property balance, the polyimidazopyrrolones (Pyrrones) developed at the Langley Research Center appeared to be one of the more promising new polymer types for potential use in a wide variety of military, aerospace, and industrial applications.

It was known that a conventional compression molding process could provide Pyrrone compactions which might find use in structural applications. However, the compression molding process was felt to be of limited practicality because of (1) the limited number of shapes that could be obtained, (2) the limitation of the specimen length-to-diameter ratios obtainable, and (3) the stress concentrations produced in a cavity mold. It was felt that these limitations might be circumvented by the

use of isostatic pressing techniques. Thus, it was the initial purpose of this program to determine the feasibility of producing useful Pyrrone compactions by isostatic pressing and to enable NASA to determine if property and/or processing advantages might accrue from the use of such processes. The appropriately precured Pyrrone prepolymers to be used in this study were to be supplied by NASA's Langley Research Center.

Isostatic compaction of powdered or granular materials is a common process in the metallurgical and ceramic industries. It has not been commonly used in forming plastics because commercially used polymers can be formed more economically in conventional molding processes. However, many of the new-generation, heat-resistant polymers have proved relatively intractable and often infusible at normal molding pressures and temperatures. Hence, there has been some experimental employment of high pressures generated in an isostatic press or autoclave to study the fabrication of these materials.

In general, isostatic pressing might be expected to provide Pyrrone compactions having the following advantages as compared to conventional compression-molded specimens:

- (1) Larger items possible.
- (2) More complex shapes possible.
- (3) More uniform compaction regardless of item shape.
- (4) More uniform density with minimized voids and air pockets.
- (5) Uniform strength in all directions regardless of item shape or size.
- (6) Lower tooling costs as a result of the potential use of disposable rubber or plastic molds.

III. SUMMARY AND CONCLUSIONS

The initial studies in this program indicated that uncured Pyrrone powders could be compacted isostatically at room temperature but that the resulting fabrications were neither thermally stable nor amenable to postfabrication cures without losing their structural integrities. Completely cured or cyclized Pyrrones could not be compacted at 100,000 psi even with liquid slip agents added. Efforts to hot isostatically compact Pyrrones were discontinued because of difficulties encountered in encapsulating the low-bulk density and non-compacting cured Pyrrone powders. Significant progress was made, however, in producing potentially useful Pyrrone fabrications by the hot compression molding process.

Compression molding procedures and conditions were determined which provide reproducible fabrications of good small-sized Pyrrone disks (1/2-inch and 5/8-inch diameter by 1/8 to 1/4-inch thickness). However, attempts to project these conditions to the fabrication of thin Pyrrone panels (3 by 4 by 1/16-inch nominal) met with varying success. Direct projection of fabrication variables seemed successful with certain Pyrrone systems in that intact panels were obtained without difficulty. Other systems appeared less adaptable in that completely intact panels were not obtained within the scope of the procedural modifications tried. These variations in process included programmed annealing to eliminate thermally induced stresses as a source of difficulty. This approach did not resolve the problem. The importance of highly controlled annealing was further discounted by pressing several panels from the mold while

still exceedingly hot. It is presently believed that much of the difficulty encountered in successful molding panels from certain Pyrrones relates to unfavorable balances of thermal expansion between the steel molds and the panels.

The general conclusions reached during this study regarding the fabricability of Pyrrones are summarized below.

- (1) Fully cured Pyrrone powders could not be isostatically fabricated to structural forms at room temperature and pressures to 100,000 psi.
- (2) Addition of liquid slip agents to fully cured Pyrrone powders did not improve their isostatic fabricability.
- (3) Uncured Pyrrone powders were successfully compacted isostatically at room temperature. Programmed cyclizations of these compactions, however, resulted in fracturing through volatile evolution.
- (4) Pyrrone powders were successfully compression molded at elevated temperatures to provide structurally useful forms.
- (5) Molding temperature appeared to be extremely critical in the compression molding of Pyrrones with best fabrications being obtained at temperatures between 520 to 530 C.
- (6) Degradation appeared to be a significant factor in molding Pyrrones at temperatures above 540 C.
- (7) Optimum molding uniformity required a finely ground Pyrrone powder free from large particles.

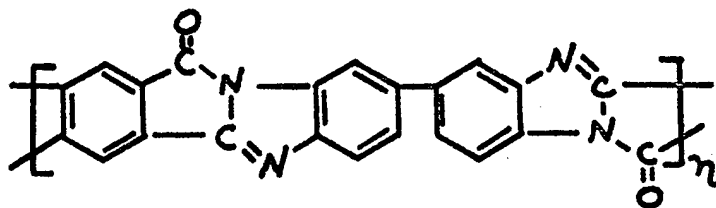
- (8) Density or microhardness measurements appeared to be suitable criteria for evaluating the qualities of molded Pyrrones.
- (9) Since the brittleness of molded Pyrrones appeared to increase with density, the attainment of moldings exhibiting a theoretical density is probably not desirable.
- (10) The thermal expansion characteristics of molded Pyrrones appeared to be such that an unfavorable mold-to-sample relationship tended to cause fracturing of the molding.
- (11) Machining procedures based upon grinding techniques appeared to be best suited for molded Pyrrones.
- (12) Although consideration was given to the possible use of Pyrrones as grinding wheel binders, the extreme brittleness of the high-temperature molded systems examined to date would seem to militate against this use.

IV. DISCUSSION OF RESULTS

Pyrrone Systems

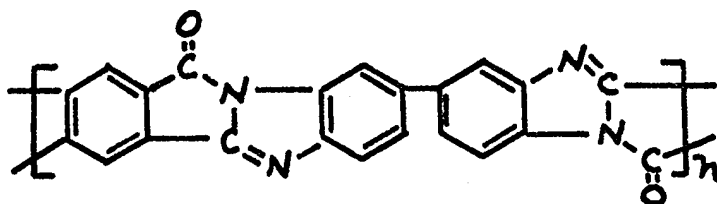
The generalized objective of this program was to determine whether the Pyrrones as a class were amenable to conventional or isostatic compression fabrication. In the implementation of this program NASA provided in powder form the following samples of four basic Pyrrone system types and variations of those systems. The polymers used in this program were the following Pyrrone systems:

System 1. Low-molecular-weight pyromellitic dianhydride (PMDA)-diaminobenzidine (DAB) made in dimethylacetamide (DMAC).



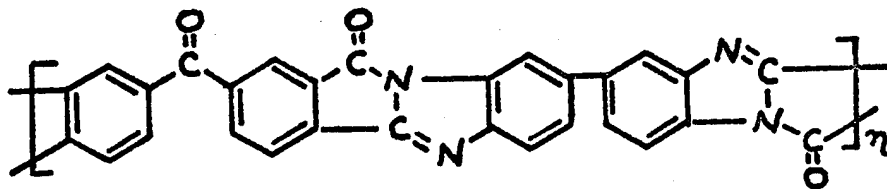
- (a) Completely cured to contain 0 percent volatiles.
- (b) Containing approximately 3 percent volatile content.

System 2. High-molecular-weight PMDA-DAB-DMAC.



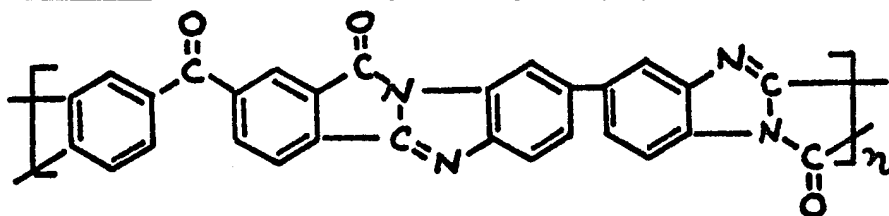
- (a) Containing approximately 0 percent volatile content.
- (b) Containing approximately 12 percent volatile content.

System 3. Benzophenone tetracarboxylic dianhydride (BTDA)-DAB-DMAC.



- (a) Containing approximately 12 percent volatile content.
- (b) Containing approximately 24 percent volatile content.

System 4. BTDA-DAB-ethylene glycol (EG).



- (a) Containing approximately 0 percent volatile content.
- (b) Containing approximately 3 percent volatile content.

Volatile-free samples and samples with 3 percent volatiles (O/V)* of Pyrrone Systems 1 and 4 provided by NASA were initially screened for susceptibility to isostatic compaction at room temperature and compression molding at 325 C (Table 1). Preliminary studies on these powders prior to molding or compaction included optical examination to assure the absence of large particles which could affect the fabricability of the systems and machinability of the compactions. Optical examination of these powders at around 30X did show some coarse particles but size and content in the molding powders were not pronounced. Initially it was not believed that powder size spread was such to militate against fabrication either by isostatic or conventional molding procedures. In order to most effectively study the fabricability of these materials, preliminary molding studies were made to establish the feasibility of the different procedures.

Room-Temperature Isostatic Pressing

Room-temperature isostatic moldings at 100,000 psi were attempted using a very simple rubber sleeve isolation chamber. Completely negative results were obtained with both the 3 percent volatile (O/V) and volatile-free samples of Pyrrone Systems 1 and 4. After isostatic pressurization

* O/V is used throughout this report for percent volatiles to avoid confusion with the volume percent (V/O) symbol.

at 100,000 psi, these samples were all recovered as uncompacted powders. Some darkening in color was noted for the NASA-1-3 O/V; otherwise, no molding or change was found. In view of these rather unexpected results, verification of the isostatic procedure was conducted with several other polymeric materials including parapolyphenylene which can be fabricated by the isostatic technique. The results showed a very acceptable compaction of the parapolyphenylene and compactations with reasonably good integrity for several other materials. As a further check on the fabricating behavior of the Pyrrone-type material, an uncured Pyrrone (EIMAC Pyrrone) was subjected to isostatic compaction. This material, unlike the NASA-supplied heat-cured samples, did compact to a cylinder with fair integrity. Initially this was a light-green powder. After compaction the material, for the most part, was black. Some small brown areas were observed under the microscope.

Compression Molding at 325 C

Fabrication studies of the Pyrrones based upon the use of heat and pressure showed somewhat more promising results (Table 1). Small amounts of powders from NASA Systems 1 and 4 were subjected to compression molding conditions (5000 psi, 325 C, for 3 hours). A small hydraulic laboratory press was used to provide the loading for the pellet fabrications. The platen temperatures were arbitrarily controlled by a Foxboro

TABLE 1. SUMMARY OF EXPLORATORY FABRICATION STUDIES

Material	Procedure	Results
NASA System 1 (before precure)	Isostatic; 25 G; 100,000 psi	Compacted; hard; fair integrity
NASA System 1 (zero volatile)	Ditto	No integrity; recovered as a powder
NASA System 1 (zero volatile with water added - 23 O/V)	"	Ditto
NASA System 1 (zero volatile, DMAC added - 23 O/V)	"	"
NASA System 1 - 3 O/V	"	Ditto; slight darkening of powder
NASA System 4 (zero volatile)	"	No integrity; recovered as powder
NASA System 4 - 3 O/V	"	Ditto
Parapolyphenylene (EIMAC 221)	"	Compacted cylinder; hard; good integrity
Polybenzimidazole ~3 O/V (Narmco-Imidite)	"	Compacted cylinder; hard; fair integrity
Polyamide-imide ~3 O/V (Westinghouse AI-131)	"	Ditto
Pyrrone (EIMAC ~30 O/V)	"	Compacted; hard; fair integrity; green powder molded to black cylinder with some brown areas. Cuts by fracture.
Ditto	"	Post-molding heating (2 hours); 17.5 percent volatiles; starts to brown.
NASA System 1	Compression 5000 psi; 325 C; 3 hours	Molded disk; integrity fails by fracture; hard surface
NASA System 1 (reground)	Ditto	Ditto
NASA System 1	Compression 35,000 psi; 325 C; 3 hours	Ditto (mold frozen--opened by machining)
NASA System 1 - 3 O/V	Compression 5000 psi; 325 C; 3 hours	Molded disk; fair integrity; fair mold surface replication; hard
NASA System 1 - 3 O/V	Compression 5000 psi; 425 C; 3 hours	Ditto; somewhat better
NASA System 4 - 3 O/V	Ditto	Disk; poor integrity; poor replication; powdery surface

controller at 300 F to reduce the heat sink effect. Heat losses were further minimized by using insulation between the platens and the pellet mold. The cylindrical mold was heated by a band heater clamped around the circumference. The temperature was monitored and controlled by a second Foxboro controller. Thermal excursions were minimized by controlling the power input to the band heater by a Variac. Heat losses were minimized by packing asbestos wool around the mold.

The compressed materials were allowed to cool slowly in the rather heavy pellet molds to minimize thermal strains. Compaction and some integrity were shown for all four systems. The volatile-free samples were rather hard friable disks which tended to fracture during removal from the mold. The fracture faces were hard and somewhat scratch-resistant. The best overall molding, however, was obtained with NASA System 1 - 3 O/V. This was recovered as a hard disk with fair replication of the mold surface. NASA System 4 - 3 O/V which was molded simultaneously with the NASA 1 - 3 O/V did not have the flow, compaction, or integrity of the latter. Since both samples were molded in the same compression mold and separated by an aluminum foil disk, it is believed that these results represent very real differences in the processabilities of the two materials under the conditions used.

Thus, the initial experimental results indicated strongly that cold isostatic compaction was not a suitable procedure for fabricating a zero or low-volatile Pyrrone. There was an indication that a high-volatile system might have properties which could permit isostatic forming. Such a fabrication, however, probably would not be thermally stable since the condensation reaction would not have been completed.

Accordingly, the overall effectiveness of the projected fabrications study, namely isostatic compaction and compression molding at 325 C of zero and low-volatile Pyrrones, appeared to be rather low. Several alternative approaches to better assess the potential of these high-temperature polymers were considered. These included:

- (1) The effect of volatile content on fabricability by heat-compression molding or isostatic treatment plus postheating procedures.
- (2) The effect of elevated temperatures on the fabricability of zero or low-volatile systems.

Consequently, it was recommended that samples of high-volatile-content Pyrrones be submitted by NASA for appropriate study.

Compaction Attempts with Slip Agents Added

A sample of System 1 before precuring (Table 1) was provided by NASA for study of fabricability. A room-temperature isostatic molding at 100,000 psi was attempted with this polymer using the simple rubber sleeve isolation chamber technique. Compaction of System 1 (green polymer) was very similar to the compaction of the EIMAC Pyrrone (green polymer). Green polymer refers to the precipitated and dried powder before the cyclization step by heating. Completely negative compaction results, however, were obtained with completely cyclized volatile-free samples of System 1 to which water and DMAC had been added. After isostatic pressurization at 100,000 psi, these latter samples all were recovered as uncompacted powders. Thus, successful room-temperature isostatic compaction of Pyrrones appeared feasible only if nonprecured powders were used. It was not likely, however, that such compactations would be

heat-resistant because they would consist of uncyclized polymer which would undergo further internal condensation reactions upon exposure to elevated temperatures. It was further believed that the volatile condensation by-products produced at elevated temperatures would disrupt the integrities of the compactions.

The isostatically compacted NASA Pyrrone (initially non-precured) was given a programmed heat treatment (Table 2). A sample of similarly compacted EIMAC Pyrrone was included in this series for comparison of behavior. Although both of these green polymer Pyrrones had similar compaction behavior, the heating sequence showed that the two were markedly different. The NASA System 1 green polymer split open during the heat program. On the other hand, the EIMAC material did not show any distortion or blowing during the heating. It is suspected that the splitting and gas-induced porosity are due to unremoved solvent since it is believed that both of these samples had the same chemical structures. We can currently offer no explanation for the fact that they would both be expected to evolve similar amounts of water of reaction during heating, yet behaved differently.

These results further confirmed that cold isostatic compaction did not appear to be a suitable procedure for fabricating a zero or low-volatile Pyrrone, even when solvent or water is added to serve as a tack or slip agent (Table 1). It was confirmed, however, that the uncyclized system does have properties which will permit cold isostatic forming. Such fabricated forms, however, are not considered to be thermally stable and useful engineering structures since the condensation reactions have not been completed.

TABLE 2. EXPLORATORY STUDIES TO DETERMINE THE EFFECT OF VOLATILE
CONTENT ON ISOSTATIC FABRICABILITY OF PYRRONES (a)

System	Post-Fabrication Form	Post-Baking Appearance (b)
1 (before cure ~23 O/V)	Dark compacted cylinder	Cylinder split by volatile pressure
EIMAC Pyrrone (before cure ~30 O/V)	Ditto	Cylinder intact; no disruptive gassing
1 (cured - 3 O/V)	Powder	Omitted
1 (cured - 0 O/V)	Ditto	Ditto
1 (cured - 0 O/V + water ~23 O/V)	"	"
1 (cured - 0 O/V + DMAC ^(c) ~23 O/V)	"	"

(a) Isostatically compacted at 100,000 psi and 25 C.

(b) Baking sequence: 1 hour at 100 C, 1 hour at 200 C, 1 hour at 300 C, and 1 hour at 400 C.

(c) Dimethyl acetamide.

Compression Molding at Extreme Temperatures

Further fabrication studies of the precured Pyrrones based upon the use of heat and pressure continued to show promising results. Small amounts of powder from NASA System 1 - 3 O/V were subjected to compression-molding conditions (325 and 425 C under 5000 psi for 3 hours). The materials were allowed to cool slowly in the heavy pellet molds to minimize thermal strains. Compaction and integrity were shown for both systems. However, it appeared that a somewhat better molding was obtained at the higher temperature.

As a result of pursuing higher temperature compression moldings of Pyrrones, a breakthrough of major significance in the production of high-quality Pyrrone compactions was made. This development appears to have been arrived at simultaneously by workers at both the Langley Research Center and Battelle's Columbus Laboratories. Literature* supporting this approach also was found shortly after the innovation was tried.

It was formerly believed that the preparation of high-density, machinable Pyrrone billets would require achieving an appropriate critical relationship with respect to the prepolymers' volatile contents, the compaction temperatures used, and the compaction pressures employed. It was also initially felt that a conventional compression molding technique would not prove satisfactory, and that the goals of the program could best be accomplished by isostatic pressing.

However, it was found that the Pyrrones could be compression-molded at pressures as low as 1000 psi if they were compacted at temperatures exceeding about 525 C. Either reactive Pyrrone prepolymer powders

* W. Grünsteidl, Kunststoffe, 58, 739-744 (1968).

or fully cyclodehydrated Pyrrones appeared to be processable with equal ease by this procedure. Pyrrone compactions of similar quality were not attainable at lower temperatures (325 and 425 C) regardless of the degree of precure of the molding powders used or the pressures applied to the powders during fabrication attempts.

In view of this development, only limited further work involving isostatic pressing seemed warranted although it was felt that some studies should, in time, be conducted to compare the effects of compression molding versus isostatic pressing on the densities of Pyrrone specimens fabricated at temperatures around and exceeding 525 C.

Exploratory high-temperature pellet moldings to determine optimum molding conditions were initiated. This work was originally restricted to volatile-free Systems 1, 2, and 4 for which a series of moldings were made at various conditions of temperature and pressure. The effectiveness of the fabricating conditions was evaluated by determining the densities of the molded samples as well as by other qualitative observations. Density evaluation during this study was based upon precision weights and volume calculated from micrometer-determined dimensions. Facilities and conditions used in this preliminary study of molding parameters were closely controlled and instrumented to provide insight into the polymer fabrication behavior and properties. Results for 1-hour moldings shown in Figure 1 suggested that the optimum molding temperatures likely would be based upon a compromise between degradation and proper flow.

Figure 2 correlates the results of pellet density with fabrication conditions for NASA Systems 1, 2, and 4. Based upon the earlier observed reduction in pellet densities for molding at 540 C, later

FIGURE 1. CORRELATION OF MOLDING CONDITIONS WITH
SAMPLE DENSITY (NASA SYSTEM 1 - VOLATILE-FREE)

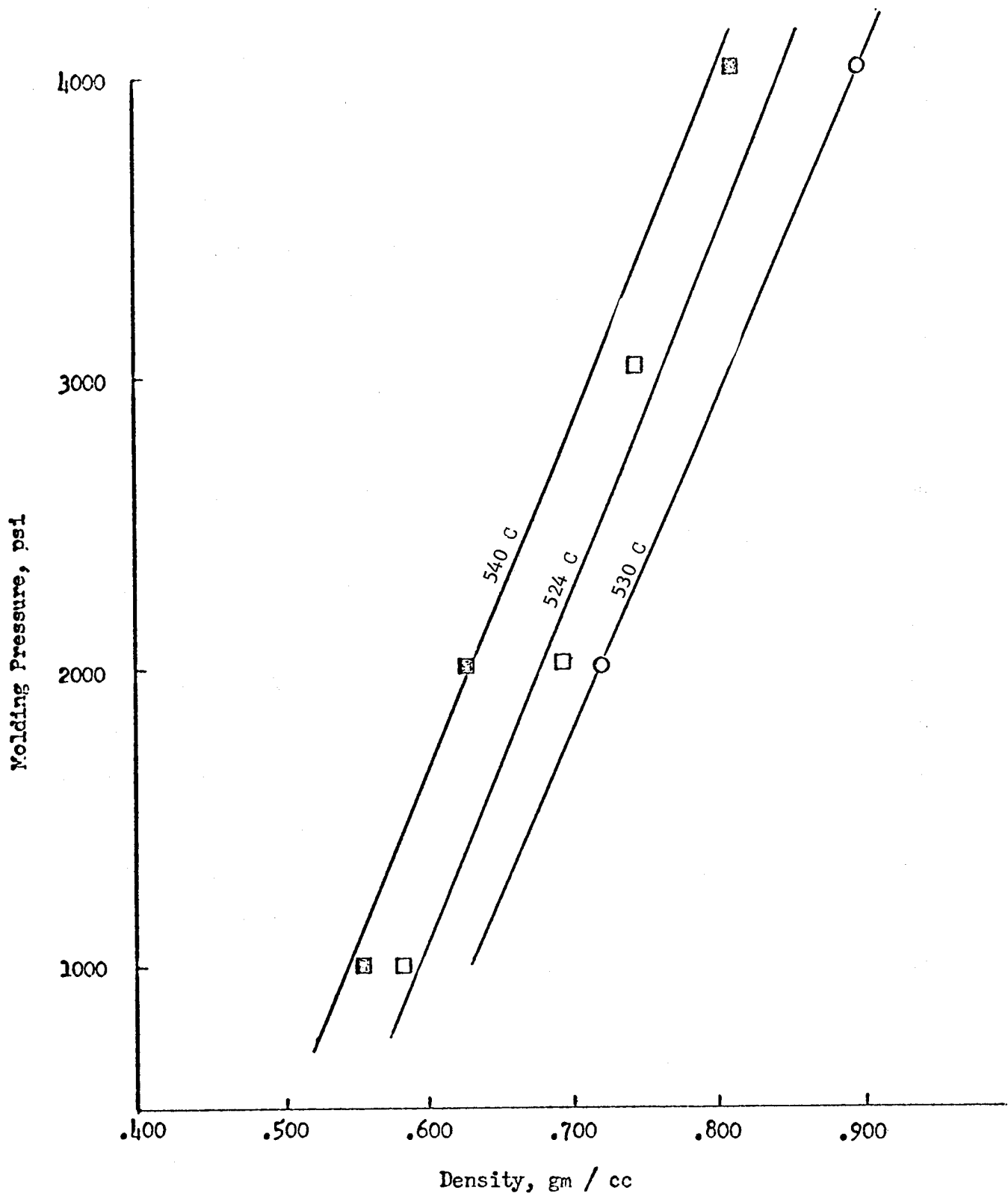
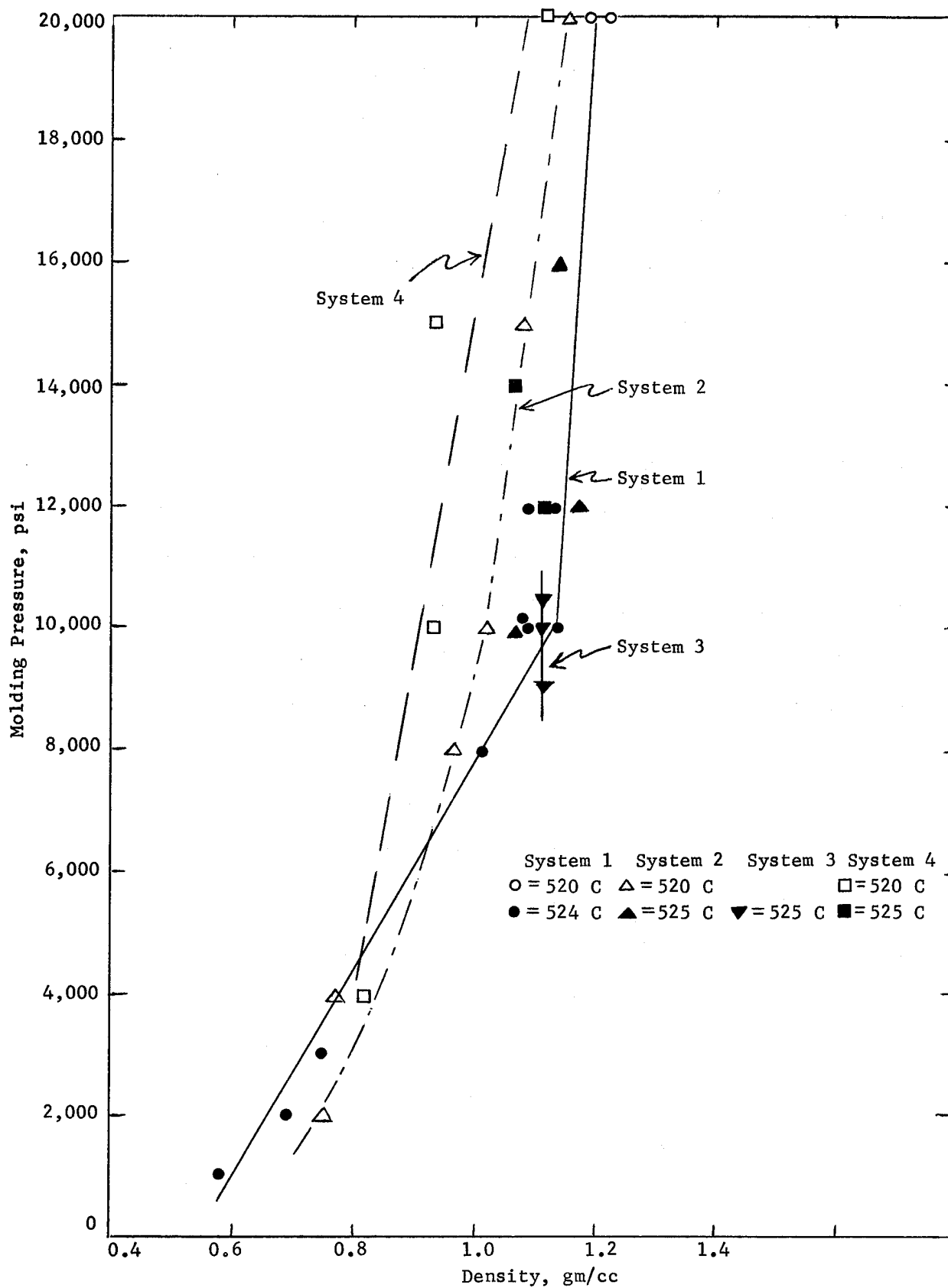


FIGURE 2. EFFECT OF PROCESSING CONDITIONS ON PROPERTIES OF COMPRESSION MOLDED PYRRONES



fabrications were made at 520 C. This temperature was arbitrarily selected for this phase of the screening study. It was believed that the slightly lower temperature might minimize the degradation and/or void formation responsible for the observed reduction in density at lower molding pressures. It seemed possible that the reactions occurring at the fabricating temperatures included both degradation and crosslinking. In this case, it seemed possible that higher molding pressures might shift the fabrication equilibrium to give slightly increased densities at the high temperatures.

The most significant aspect of the data relating to the processing of these systems appeared to be differences in compacting behavior. Although some spread exists in the data, it was believed that these general compaction patterns and temperature-induced differences were real. It was not known whether the differences in compactibility at a given temperature were related to the structural differences of the polymers or to particle size factors. It was believed, however, that the polymer structural factors were likely responsible for differences in viscous flow and possibly degradation and crosslinking which occurs in the compacted pellet. It is interesting to note that pressures around 35,000 to 40,000 psi appeared to be required to produce compactions with near theoretical density (about 1.4) for these systems.

It was subsequently found that additional grinding of the Pyrrone systems made possible the production of moldings that were significantly more homogeneous than those prepared earlier. In addition, the hardness characteristics of Pyrrone moldings were defined as a guide for specimen fabrication.

Density characterizations indicated that pressures of about 40,000 psi at 525 C were required for the production of Pyrrone moldings having near-theoretical densities. However, such moldings tended to be extremely brittle and shock-sensitive. Accordingly, thought was given to compromise conditions which might result in samples which would have less critical handling and testing properties. Since, in general, brittleness increased with hardness, consideration was given to the possibility of producing somewhat less hard and brittle specimens.

To explore this possibility, the hardness values of all available samples were measured. The initial attempts to obtain Rockwell measurements resulted in fractures of the molded buttons. Consequently, the subsequent measurements were made on a Wallace Micro Indentation Tester*. This device is designed to measure the hardness values of rigid and semirigid plastics. The instrument consists of a Vickers pyramid diamond indenter and a means for applying a primary (1 gram) and a secondary load (300 grams) to it. Indentation is measured by determining the depth of penetration produced in 15 seconds by the secondary load.

The results of these hardness characterizations are shown in Figures 3 through 5. It is interesting to note that the hardness pattern for fabrication conditions appears somewhat different from the density pattern obtained earlier. Hardness values appeared to increase at a fairly constant and significant rate with pressure in the range studied.

* Testing Machines, Inc., Wallace Micro Indentation Tester, Model H-6.

FIGURE 3. EFFECT OF PROCESSING CONDITIONS ON PROPERTIES OF COMPRESSION MOLDED PYRRONE (SYSTEM 1)

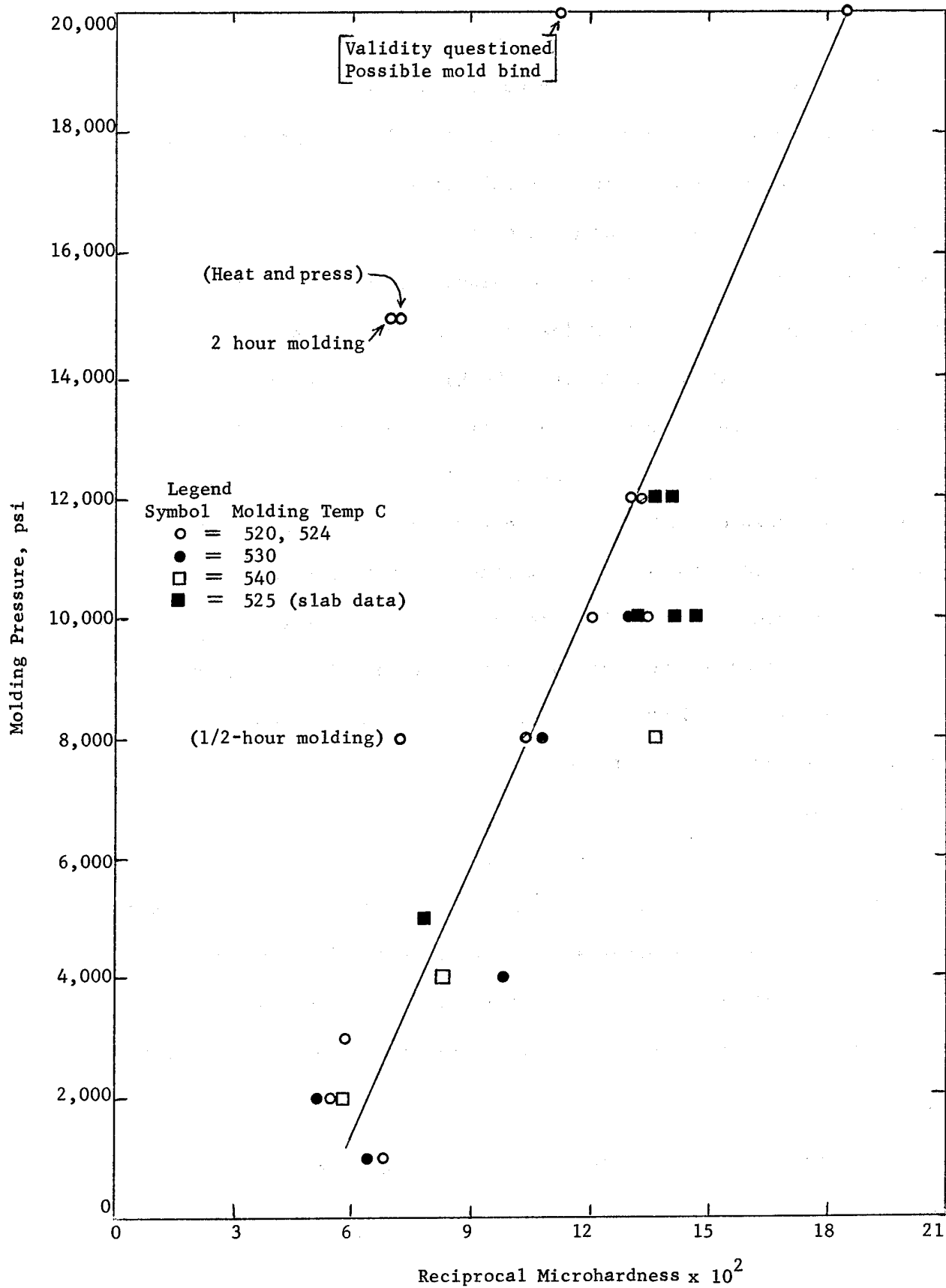


FIGURE 4. EFFECT OF PROCESSING CONDITIONS ON PROPERTIES OF COMPRESSION-MOLDED PYRRONES (SYSTEM 2)

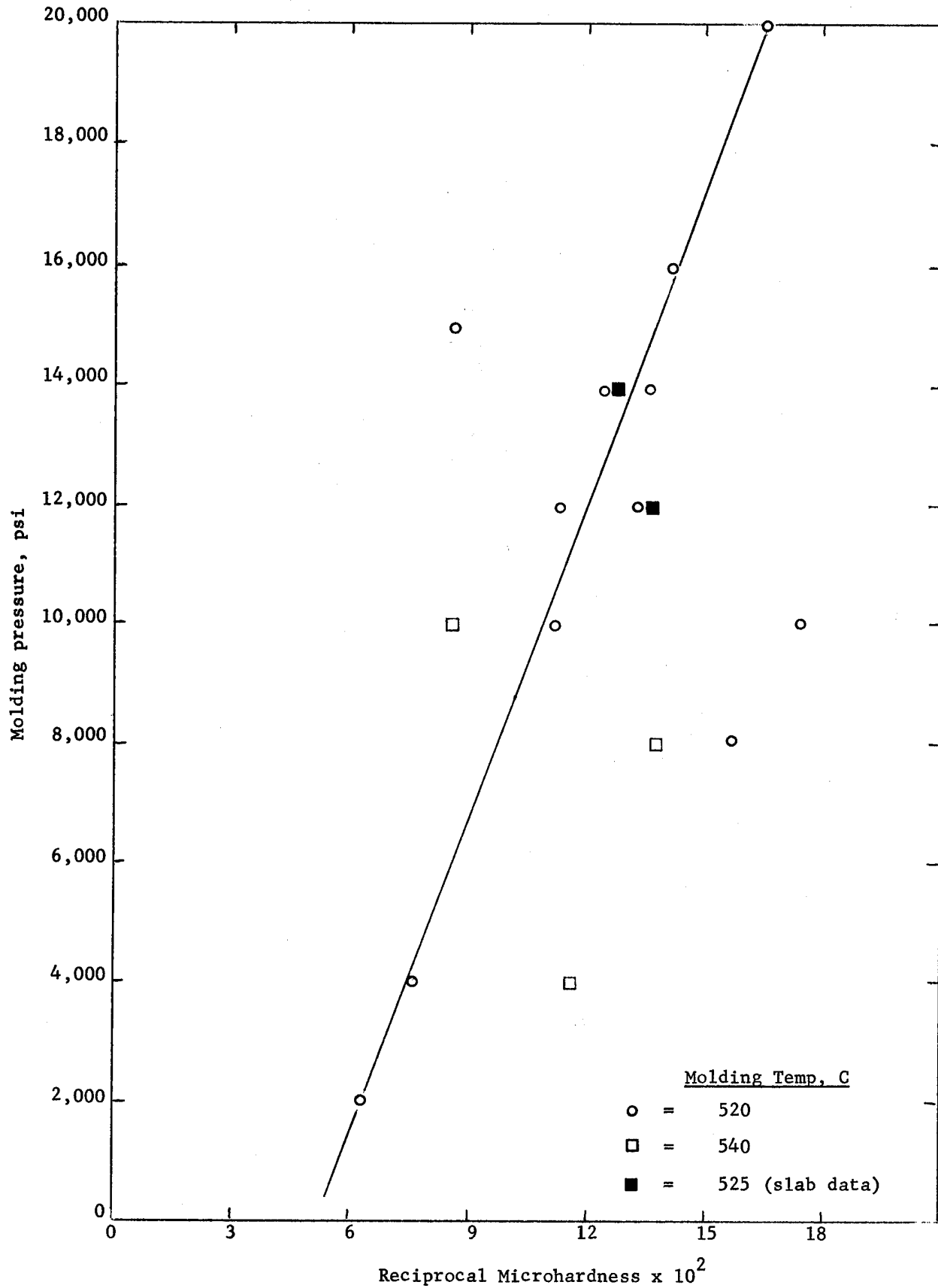
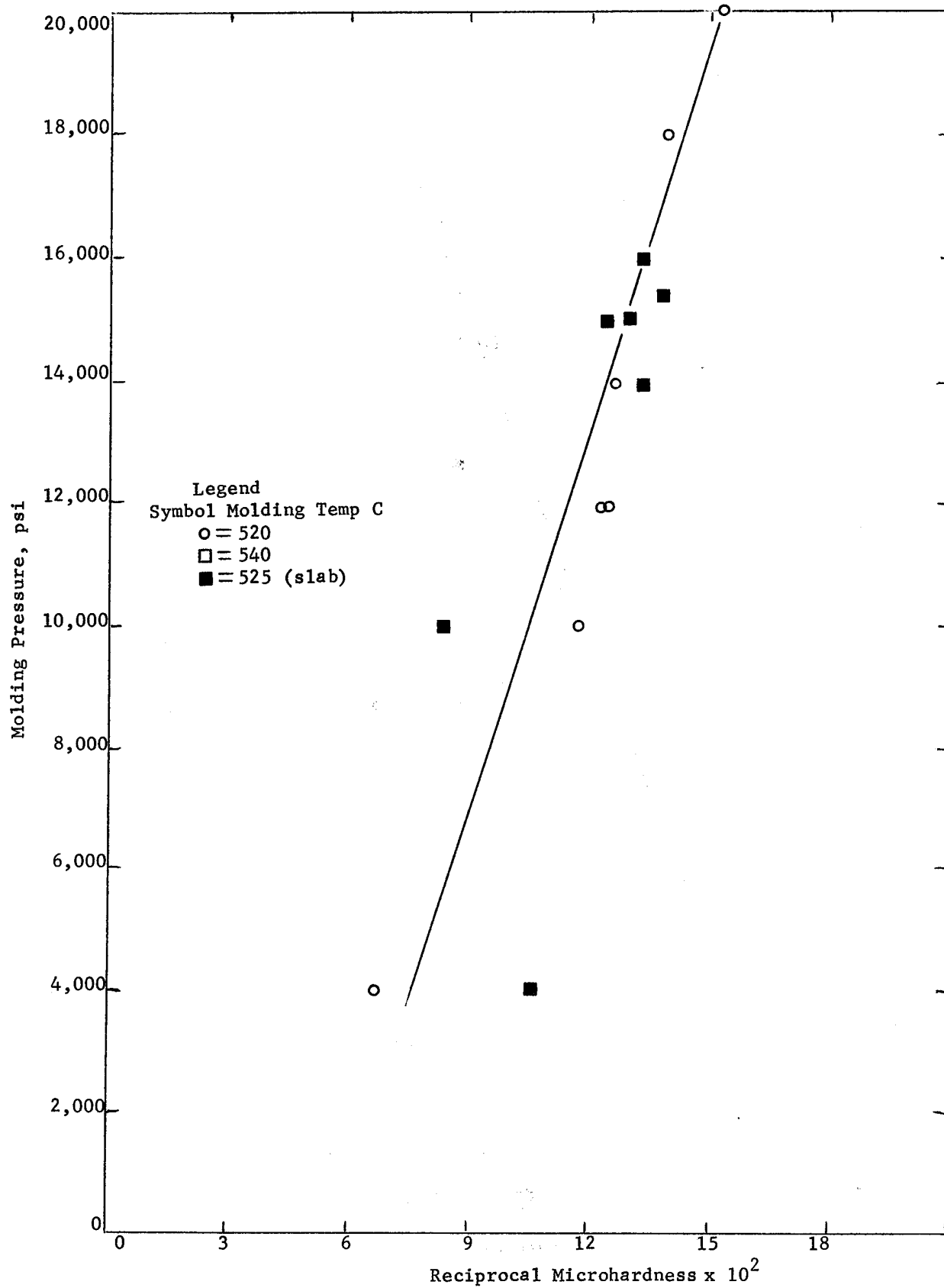


FIGURE 5. EFFECT OF PROCESSING CONDITIONS ON PROPERTIES
OF COMPRESSION MOLDED PYRRONE (SYSTEM 4)



Although considerable spread is shown in the hardness data, an attempt was made to project the general trend for the various systems based upon the results of moldings in the range of 520 to 525 C. There appeared to be only slight differences in the hardness response to molding conditions for the systems shown. Since a number of factors could affect the validity of the hardness results, it seems presumptuous, in the absence of statistically valid molding data, to draw conclusions relative to the fabricability of the various systems. It is suspected, however, that for most practical purposes, the hardness-molding correlations are virtually the same for these systems.

It is known that several factors can affect the validity of the results used in the hardness-molding correlations. As indicated previously, one of these is the loss in internal molding pressure from frictional forces between the piston and the cylinder of the mold. Since the internal pressure is projected from the load-piston area, a loss in fabrication pressure would be reflected as a soft material at high pressure.

Effect of Grinding on Homogeneity

Another factor known to significantly affect the hardness characterization is the Pyrrone grind. Marked color differences were noted in a pellet molded from System 1 containing 3 percent volatiles. The use of the microhardness tester was effective in establishing that the different shades showed different hardness values. In addition, a variation in composition could be observed in the powders under microscopic examination.

Further ball-milling of an aliquot sample of System 1 appeared helpful in improving the uniformity of the powder by microscopic examination, and the appearance and hardness uniformity of a pellet molded

from it. The results in Table 3 show the hardness variations for these systems and the improvement realized by grinding.

Thought had been given to the possible potential of the Pyrrones as binders for grinding and cutting wheels. A reference* was found that discussed the properties of polyimides used in this application. According to data on the SP polymer, the hardness values run around 90 Rockwell H. SP polymer samples readily available were checked and found to have Rockwell H values of 89 and 92. These samples had microhardness values of 0.00076 and 0.00073, respectively. (Reciprocal microhardness values are 13.15×10^2 and 13.70×10^2 , respectively.) Accordingly, it was planned to attempt to mold Pyrrone samples to similar hardnesses for evaluation. It was not known whether this level of hardness would provide the desired reduction in brittle behavior but qualitative observations of fracture and grinding behavior indicated that an improvement in properties might be expected.

Based upon previous experience, all of the Pyrrone systems were subsequently ball-milled prior to pellet molding and slab fabrication (Table 4). Grinding was routinely carried out for 22 hours on fast rolls using ceramic elements (3/4 inch long by 3/4 inch diameter) in a ceramic jar.

Slab Molding Procedures

Slab fabrication (as well as pellet molding) utilized two thicknesses of 7628 glass cloth on both faces of the charge. This was a relatively light cloth (5.80 ounces/square yard). It was a square weave with nearly balanced construction (42 by 32). The fabric was

* Carl H. Jepson, "A New Development in Bonded Abrasive Products", Proceedings of International Industrial Diamond Conference, Oxford, England, June, 1967.

TABLE 3. INVESTIGATION OF HARDNESS VARIATIONS IN MOLDED PYRRONES

System	Reciprocal Microhardness $\times 10^{-2}$ (a)				Molding Conditions		Comments
	Maximum	Minimum	Average (b)	Standard Deviation, percent (b)	Temp, C	Pressure, psi	
1 Side 1 (c)	5.88	6.50	6.13	4.4	520	15,000	Powder as received, zero volatiles
Side 2	7.68	10.4	8.76	12.1			
1 Side 1	12.05	15.15	13.52	8.5	525	12,000	Powder as received, 3 percent volatiles
Side 2	10.20	14.30	12.53	13.6			
1 Side 1	12.35	13.00	13.12	5.3	525	10,000	Powder ball-milled 22 hrs, zero volatiles
Side 2	14.30	14.52	13.65	4.7			

(a) Microhardness methods measure penetration.

(b) Based on six determinations.

(c) Side 1 and Side 2 used to indicate opposing faces of molded pellet.

TABLE 4. SUMMARY OF SELECTED PRELIMINARY MOLDING STUDIES

System	Volatiles, percent	Pressure, psi (a)	Density, g/cc	Reciprocal Microhardness $\times 10^{-2}$				Std. Dev.	Comments
				Side	(b)	Max.	Min.	Ave.	
1	0	10,000	1.106	1	12.35	14.30	13.10	5.3	Material ground 22 hours in ball mill
				2	13.00	14.50	13.63	4.7	
1	3	12,000	1.104	1	13.15	13.70	13.42	1.4	Material ground 22 hours in ball mill
				2	13.00	13.70	13.40	2.6	
2	0	12,000	-	1	11.00	12.82	11.60	5.2	Material ground 22 hours in ball mill
				2	10.10	11.75	11.25	5.8	
2	0	14,000	-	1	11.78	13.15	12.47	5.7	Material ground 36 hours in ball mill
				2	11.78	13.32	12.40	4.5	
2	0	16,000	1.137	1	13.52	14.70	14.18	3.6	Material ground 80 hours in ball mill
				2	13.70	14.70	14.25	2.9	
2	0	14,000	1.123	1	13.15	14.50	13.80	3.7	Material ground 80 hours in ball mill
				2	13.0	14.30	13.45	3.6	
2	12	10,000	1.076	1	10.20	12.82	11.05	7.9	As received powder
				2	9.80	14.30	11.28	12.7	
2	12	12,000	1.169	1	12.50	14.95	13.42	5.3	Material ground 22 hours in ball mill
				2	12.35	15.15	13.52	6.8	
3	12	10,000	1.118	1	11.63	13.50	12.68	5.6	As received powder
				2	11.48	13.50	12.60	5.8	
3	12	10,500	1.112	1	13.32	14.50	13.76	3.1	Material ground 22 hours in ball mill
				2	13.50	15.62	14.25	4.7	
3	12	9,000	1.117	1	13.0	13.90	13.52	3.0	Material ground 76 hours in ball mill
				2	13.32	14.30	3.70	2.4	
3	24	10,000	1.118	1	12.05	14.92	13.40	7.1	Material ground 22 hours in ball mill
				2	13.16	15.62	13.77	5.6	
4	0	12,000	1.104	1	12.35	12.50	12.38	0.5	Material ground 22 hours in ball mill
				2	12.20	12.82	12.44	2.3	
4	0	14,000	1.062	1	12.50	13.00	12.73	1.7	Material ground 22 hours in ball mill
				2	12.20	13.00	12.55	2.2	
4	0	18,000	1.151	1	13.32	14.50	13.90	3.1	Material ground 22 hours in ball mill
				2	13.70	14.50	14.12	2.4	
4	3	10,000	1.083	1	11.48	12.05	11.73	1.7	Material ground 22 hours in ball mill
				2	11.48	12.20	11.85	2.4	
4	3	12,000	1.111	1	12.20	12.50	12.38	0.9	Material ground 22 hours in ball mill
				2	12.20	12.66	12.35	1.4	

(a) Molding temperature 525 C; molding time 1 hour.

(b) Side 1 and Side 2 used to indicate opposing faces of molded pellet.

sprayed with silicone release agent to facilitate stripping. The release coating was air-dried before assembly. Cloth preforms were cut as precisely as possible to conform to a 4 by 3-inch mold. This was to minimize heavy cross sections of material along the walls of the mold. The initial slab runs used a sheet of 1/32-inch asbestos in place of the glass cloth next to the mold face. This procedure was used to provide gas bleeding, compression equalization, and thermal insulation to facilitate annealing. However, this assembly resulted in heavy wall cross sections which seemed to bind on the mold and promote slab fracture. In addition, inclusions in the asbestos produced pits in the moldings deeper than the normal cloth weave. Asbestos paper mold facing accordingly was discontinued in favor of a second ply of glass cloth.

Slab molding procedures and conditions (Table 5) initially followed as closely as possible the procedure used in pellet molding. The heating period in the latter was about 15 minutes to reach the molding temperature. This rapid heating was obtained in a relatively small cylinder using a band heater. Similar heating periods in the slab moldings were obtained by preheating the platens before inserting the mold. Platen temperatures for the slab moldings were individually controlled by Foxboro controllers. Mold temperatures were monitored by a portable potentiometer. The thermocouple was installed in the side of the mold to a depth near the edge of the panel. The entire assembly was surrounded by several inches of asbestos wool to minimize heat loss through the edges of the compression mold.

A 140-ton hydraulically operated Watson-Stillman press was used to load the compression molds. The desired pressures were maintained by

TABLE 5. SUMMARY OF PYRRONE FABRICATION STUDIES

Run No.	System	Volatiles, percent	Preheat Schedule (a) Time, min.	Fabrication Conditions (b)			Panel Appearance (d)	Comments
				Load, tons	Pres. Equiv., psi	Annealing (c) Time, min. Temp., C		
1	1	0	22	60	10,000	105	200	Cracked, some pits (e)
2	1	0	20	60	10,000	110	175	Broken (e)
3	1	0	18	60	10,000	--	--	Broken (e)
4	1	0	18	60	10,000	150	140	Intact (f)
5	1	3	17	72	12,000	150	140	Cracked (f)
6	1	3	17	72	12,000	150	140	Intact
7	2	12	17	72	12,000	150	140	Intact
8	3	12	17	60	10,000	150	140	Broken
9	3	24	17	60	10,000	150	140	Broken
10	4	3	16	84	14,000	210	121	Cracked (6 pcs)
11	4	0	16	96	16,000	240	125	Highly fractured
12	4	3	16	92	15,400	240	130	Cracked (7 pcs)
13	4	3	21	96	16,000	220	147	Highly fractured
14	4	3	22	90	15,000	220	152	Cracked (3 pcs) (g)
15	3	12	22	54	8,800	220	152	Highly fractured (g)
16	3	12	22	54	8,800	220	164	Highly fractured (h)

Maximum temperature 535, reduced to 525 C. Heater trouble after 25 minutes

Mold heated to 300 C, relay failed, run continued after repair

Preheat contact ~ 5 tons, released

Same preheat procedure as 3

Ditto

"

"

"

Preheat contact ~ 18 tons, released

Programmed cooling ~ 1 C/min

Programmed cooling ~ 1 C/min; panel pressed out ~ 120 C

Programmed cooling ~ 1 C/min; panel pressed out ~ 120 C

Programmed cooling ~ 1 C/min; panel pressed out ~ 135 C

Programmed cooling ~ 1 C/min; panel pressed out ~ 120 C

Programmed cooling ~ 1 C/min; panel pressed out ~ 120 C

TABLE 5. (Continued)

Run No.	System	Volatiles, percent	Preheat Schedule (a) Time, min	Fabrication Conditions (b)		Annealing (c) Time, Temp., min. C	Panel Appearance (d)	Comments
				Load, tons	Pres. Equiv., psi			
17	4	0	24	90	15,000	28	Intact	Panel removed hot--retained between metal faces for nominal annealing
18	3	24	22	60	10,000	28	Cracked (4 pcs)	Ditto
19	3	24	22	60 (14)(i)	10,000	28	Cracked many pcs	"
20	2	0	22	84 (16)	14,000	28	Cracked (4 pcs)	"
21	3	24	23	60 (15)	10,000	--	Cracked 1 large pc	"
22	3	12	22	54 (15)	8,800	--	Cracked (5 pcs)	"

(a) Normal procedure consisted of preheating the press platens to about 450 C before inserting mold. This gives a preheat period to reach 525 C comparable to the pellet studies.

(b) Fabrication was standardized at 525 C for 1 hour under the loading projected to give a microhardness of about 0.00075.

(c) Samples were permitted to cool under pressure with insulation intact to reduce stress effects from thermal shock. Panels normally pressed from mold at room temperature. Exceptions noted.

(d) Normal panel construction consisted of two plies of 7628 glass cloth on each face. Exceptions noted.

(e) Two sheets of asbestos (1/32 inch) and one Sheet 7628 each face.

(f) One sheet of asbestos (1/32 inch) and two Sheets 7628 each face.

(g) Normal glass facing; asbestos ring around molding to isolate panel from cavity wall.

(h) No facing material used.

(i) Load applied at time shown in parenthesis.

setting the by-pass control to maintain the required press loads. Some compaction of the charge was attempted after installation in the press. This involved pressurization to a low loading followed by pressure release. No further load was applied until the fabrication temperature was reached. At this time the load was applied to produce a compaction projected to an indentation penetration falling between 0.00073 and 0.00076 (the reciprocal microhardness ranges from 13.7 to 13.2×10^2 , respectively).

A total of 22 slab runs was made from which four intact panels (3 by 4 by 1/16-inch nominal) were recovered. These include System 1 - no volatiles, System 1 - 3 percent volatiles, System 2 - 12 percent volatiles, and System 4 - no volatiles. Pellets (5/8-inch diameter), however, could be molded from each of the Pyrrone systems submitted. It was known from the pellet studies that the Pyrrones were quite brittle. In view of this property, the slab fabrication approach using a large area and small thickness undoubtedly was exceedingly sensitive to thermal excursions, fabric-induced stresses and, very likely, decompression parameters. In view of the fairly reproducible success in the pellet molding, a number of variations in panel molding procedures were explored to try to improve panel recovery. Although insulation and pressure were retained on the earlier panel samples to provide a nominal annealing effect, it was considered likely that thermal stresses were induced during the relatively short (2-hour) period in which the samples cooled from 525 C to about 150 C.

Accordingly, several moldings were made in which the cooling rate was controlled to about 1 C per minute. However, panels pressed

out at room temperature still were either cracked or highly fractured. These results appeared to discredit the importance of annealing in preventing panel breakage.

Consideration was next given to the possibility of thermally induced compressive stresses causing the breakage. Generally, the coefficients of thermal expansion for polymeric materials are considerably greater than those of metals. This shrinkage results in facilitating the removal of plastic parts from molds. The possibility of an adverse thermal expansion relationship was checked by refrigerating a pellet molding in a freezer. This was driven from the mold while still quite cold. This pellet was badly fractured on recovery. Further confirmation of the presence of an adverse thermal expansion relationship was obtained by demolding panels at elevated temperatures. System 4 which was always recovered as a cracked or fractured panel was obtained intact by demolding near the fabrication temperature. Nominal annealing was obtained by keeping the panel between the mold faces and covering the assembly with insulation. Measurement of this panel and the mold cavity after both had been cooled to room temperature revealed the panel was about 10 to 12 mils larger on a side than the mold. Although other factors such as moisture absorption can cause swelling, it presently seems likely that the panel cracking observed is due to compressive failure during cooling. The geometry of this sample will be quite vulnerable to this loading since it is essentially a small, unsupported column after the press pressure is removed. Furthermore, cracking is considerably more pronounced on the longer side. Based upon these rather surprising results, Pyrrone parts and fabrication facilities will need to be designed to minimize this

effect. Thus, although compression molding fabricability of the Pyrrones has been verified, thermal expansion behavior may relate better to hot isostatic techniques. Here, a relatively thin-walled container would be free to follow the dimensions of the sample. This, however, would entail the use of a partially compressed and stabilized preform which could be satisfactorily sealed in a can. Earlier work on the use of isostatic techniques ran into difficulty in this encapsulation step.

A summary of the Pyrrone samples (2 by 1/2 by 1/16-inch nominal) supplied is presented in Table 6 with data to show microhardness and the source of the polymer used in each panel run. Adequate samples were obtained for Systems 1 and 4 at both volatiles level and for System 2 at 12 percent volatiles and System 3 at 24 percent volatiles. About half of the desired samples were obtained for System 2, zero volatiles and 3 at 12 percent volatiles.

Pyrrone Machining Procedures

Initially, a band saw was used for sectioning the intact panels. A medium blade and medium speed were reasonably satisfactory. However, even under the best conditions, some chipping was encountered. Also, this procedure gave an irregular cut which would require further finishing. Accordingly, the best procedure for fabrication of these materials seemed to be based upon grinding techniques. The panels were sectioned into 1/2 by 2-inch specimens using a 1/16-inch-thick carborundum cut-off wheel in a high-speed rubber grinder. The depth of cut in each pass was quite small (about 2 mils) to prevent panel damage. Similar precautions were used during surface grinding of the samples on the same unit using a 1/2-inch-wide grinding wheel. First, passes were about

TABLE 6. SUMMARY OF SAMPLES SUPPLIED (a)

Run Number	System Number	Volatiles Content	Reciprocal Microhardness, Ave. x 10 ⁻²			Comments
			Minimum	Maximum	Average	
4	1	0	14.06	12.82	13.45	Twelve pieces 2 x 1/2 x 1/16-inch nominal
6	1	3	14.94	13.00	13.77	Ditto
7	2	12	14.94	12.65	13.63	"
1	1	0	14.94	10.52	13.28	Eight pieces 2 x 1/2 x 1/16-inch nominal, balance of broken panel
2	1	0	15.15	12.82	14.28	Ditto except three pieces
3	1	0	16.38	12.20	13.88	Ditto except one piece
5	1	3	14.70	11.90	13.65	Ditto except six pieces
8	3	12	15.15	13.34	14.22	One piece 2 x 1/2 x 1/16-inch nominal
15	3	12	--	--	--	No pieces
16	3	12	--	--	--	No pieces
9	3	24	--	--	--	No pieces
10	4	3	14.06	12.65	13.44	Five pieces 2 x 1/2 x 1/16-inch nominal
12	4	3	14.28	13.55	13.95	Two pieces 2 x 1/2 x 1/16-inch nominal
13	4	3	14.70	12.65	13.50	Two pieces 2 x 1/2 x 1/16-inch nominal
14	4	3	14.50	12.05	13.10	Six pieces 2 x 1/2 x 1/16-inch nominal
11	4	0	--	--	--	No pieces
17	4	0	13.10	11.92	12.45	12 pieces 2 x 1/2 x 1/16-inch nominal
18	3	24	14.22	12.78	13.35	Four pieces 2 x 1/2 x 1/16-inch nominal
19	3	24	--	--	--	No specimens; badly fractured
20	2	0	13.50	12.10	12.68	Five pieces 2 x 1/2 x 1/16-inch nominal
21	3	24	15.78	14.15	15.05	Six pieces 2 x 1/2 x 1/16-inch nominal
22	3	12	15.15	13.64	14.35	Four pieces 2 x 1/2 x 1/16-inch nominal
<u>Summary of Runs by Systems</u>						
	1	0				24 pieces 2 x 1/2 x 1/16-inch nominal
	1	3				18 pieces 2 x 1/2 x 1/16-inch nominal
	2	0				5 pieces 2 x 1/2 x 1/16-inch nominal
	2	12				12 pieces 2 x 1/2 x 1/16-inch nominal
	3	12				5 pieces 2 x 1/2 x 1/16-inch nominal
	3	24				10 pieces 2 x 1/2 x 1/16-inch nominal
	4	0				12 pieces 2 x 1/2 x 1/16-inch nominal
	4	3				15 pieces 2 x 1/2 x 1/16-inch nominal

(a) All amples sectioned and ground to 1/16-inch nominal.

2-3 mils but this was reduced to about 1 mil as the cloth pattern was removed.

The unit used in the sectioning and grinding of these samples was a Sanford Manufacturing Corporation high-speed rubber grinder. Pyrrone panels were held on steel plates with double-faced tape during sectioning and surfacing. The grinder was equipped with a magnetic bed capable of precision positioning with micrometer attachments.

V. RECOMMENDATIONS

- (1) The effects of mold design and sample geometry should be studied to determine parameters necessary for recovery of unfractured Pyrrone moldings.
- (2) Techniques should be developed for encapsulating Pyrrones in metal cans for hot isostatic molding to determine whether this method could routinely provide unfractured samples.
- (3) The production of alloys of Pyrrones with other heat-resistant polymer types should be explored to determine if materials that are Pyrrone-based and retain many of the outstanding properties of the Pyrrones, but having improved fabricability, can be achieved.